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# Thermophysical Properties of Six Solid Gun Propellants

by Martin S. Miller

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## **Thermophysical Properties of Six Solid Gun Propellants**

**Martin S. Miller**

Weapons and Materials Research Directorate, ARL

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## Abstract

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Measurements are reported of the thermal conductivities and thermal diffusivities of six U.S. Army solid gun propellants over the temperature range -20C to +50C at atmospheric pressure. The propellants are members of the BRL research series propellants that have been widely distributed to research laboratories in the U.S. These propellants include representative types from each class of materials that are either in the fielded inventory or experimental ("X" prefix), i.e., a single base (M10), a double base (M9), a homogeneous triple base (JA2), a composite triple base (M30), a composite nitramine with inert plasticizer (XM39), and a composite nitramine with energetic plasticizer (M43). Conductivities and diffusivities were measured simultaneously using a new experimental technique developed specifically for the purpose. The experiment is designed to approximate the mathematical idealization of a one-dimensional, infinite, two-component, composite solid whose planar interface is subjected to a step-function heat flux. The average values obtained are estimated to be accurate to within  $\pm 5\%$ , and least-squares polynomial fits are provided for convenient use of the data in calculations. For convenience, a table is given summarizing the polynomial fits from the present measurements and from previous measurements of the specific heats for the same propellant lots.

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## 1. INTRODUCTION

Thermal transport properties of unreacted solid propellants play an important role in determining how much of the chemical energy release is retained in the reaction zones and, in turn, the rate of combustion and surface regression. Notwithstanding this obvious relevance to combustion modeling as well as to calculations of ignition, cookoff, and environmental temperature accommodation, few measurements of these properties have been published for solid propellants in general. Moreover, we have been unable to find any published data at all for solid *gun* propellants in particular. This deficiency, in part, may be due to the experimental difficulties attending the measurement of transport properties using small test specimens. With gun propellants one is generally limited to specimens of linear dimensions on the order of half a cm, but small specimens are also desirable for explosives and rocket propellants from a safety standpoint. This report documents simultaneous measurements of thermal conductivity and thermal diffusivity of six solid gun propellants over the temperature range of  $-20^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$  using a newly developed experimental technique appropriate for such small specimens (Miller and Kotlar, 1993). The propellants studied constitute the BRL Research-Series Propellants, a quantity of single-batch, standard Army gun propellants manufactured specifically for advanced combustion-mechanism research. This group of propellants includes examples of each different type of propellant formulation currently of interest: M10 (single base), M9 (homogeneous double base), JA2 (homogeneous triple base), M30 (composite triple base), and XM39 (composite nitramine). In addition to providing needed data for combustion-mechanism research on these particular materials, the data should enable rational estimates of the thermal transport properties to be made of other propellants with similar ingredients. Measurements of the specific heats of these same propellants over the temperature range  $-40^{\circ}\text{C}$  to  $75^{\circ}\text{C}$  are reported elsewhere (Miller, 1992a). A table summarizing the polynomial fits to thermal diffusivity, thermal conductivity, and specific heat for all of these propellants is given at the end of this report. With the exception of M43, these data have also been published in the open literature (Miller (1994a), Miller (1994b)).

## 2. EXPERIMENTAL TECHNIQUE

The design of the experimental fixture and the data-reduction procedures are discussed and justified at length in a separate paper (Miller and Kotlar, 1993). Here we provide a short summary of the technique for coherence and completeness. In essence the experiment is designed to approximate closely the mathematical idealization of two one-dimensional semi-infinite solids separated by the plane  $x = 0$ , which is subjected to a step-function heat flux at  $t = 0$ . The exact solution to the heat-conduction equation for the temperature at some distance  $x$  from the source plane at some time  $t$  is given by Carslaw and Jaeger (1959),

$$T = T_0 + \left( \frac{2f_0\lambda\sqrt{\alpha_b}}{\lambda\sqrt{\alpha_b} + \lambda_b\sqrt{\alpha}} \right) \sqrt{\alpha t} \operatorname{ierfc} \left( \frac{x}{2\sqrt{\alpha t}} \right)$$

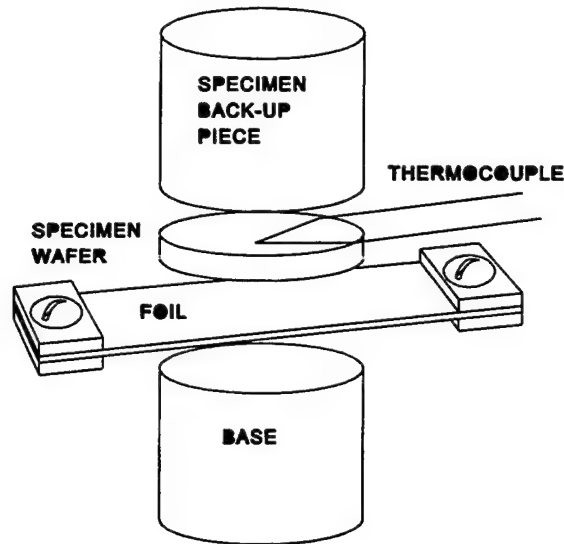
where the test material is assumed to occupy the region  $x > 0$ , the *base* material of known thermal properties occupies the region  $x < 0$ ,  $\alpha$  and  $\alpha_b$  are the thermal diffusivities of the test material and the base respectively,  $\lambda$  and  $\lambda_b$  are the thermal conductivities of the test material and base,  $T_0$  is the initial temperature everywhere at  $t = 0$ , and  $f_0$  is the magnitude of the heat flux for  $t > 0$ .

Experimentally, the step-function heat flux is generated by the sudden application of a constant voltage to a thin resistance foil located at the interface of the two "semi-infinite" solids. If the current established in the foil is  $I$ , its electrical resistance  $R$ , its length  $L$ , and its width  $W$ , then the heat flux is given by

$$f_0 = \frac{I^2 R}{LW}$$

The ideality with which a step-function current in a foil can produce a step-function heat flux has been thoroughly discussed by Miller (1992b), who derived an exact Laplace-transform solution to the problem of a finite-thickness foil. The finite heat capacity of the foil delays the attainment of a constant heat flux even when the current in the foil is a perfect step function. This effect is minimized by using very thin foils. In the measurements reported here a Constantan foil 5- $\mu\text{m}$  thick

is employed, resulting in errors in the thermal conductivities and diffusivities of less than 2% due to non-idealities in the step-function heat flux.



**Figure 1. Exploded schematic view of experimental arrangement of test specimen pieces and heat-flux-generating foil.**

Fig. 1 shows a schematic representation of the experimental setup. In reality, the foil is wider than the specimen diameter and thermal guards are employed. Voltage from a regulated DC supply is applied to the foil by means of a mercury-wetted relay. The temperature as a function of time (up to about 4 s) is then measured in the test specimen at a distance of about 0.5 mm from the foil by means of a 5- $\mu$ m-thick Chromel-Alumel foil-type thermocouple interposed between a test-specimen wafer and a test-specimen back-up piece. The back-up piece is about 0.65 cm long which is sufficiently long to give temperatures that differ from an infinitely thick piece by less than 1%. The many conditions for the experiment to closely approximate the mathematical idealization embodied in Eq. 1 are analyzed in detail by Miller and Kotlar (1993). A determination of the thermal

conductivity  $\lambda$  and diffusivity  $\alpha$  is then made by performing a non-linear least-squares fit of Eq. 1 to the data using  $\lambda$  and  $\alpha$  as fitting parameters. Temperature conditioning of the copper conductivity/diffusivity fixture was accomplished by means of ethylene glycol circulated from a temperature-controlled bath through copper tubing soldered to the fixture. A mineral-fiber insulation jacket thermally isolated the fixture from its environment.

### 3. PROPELLANT DESCRIPTIONS

All the tested propellants were extruded with a diameter close to 6.4 mm. Specimen wafers were cut to a thickness of about 0.5 mm with a low-speed, diamond-bladed wafering saw using water as a coolant. This saw produces smooth, low distortion cuts and wafers of very uniform thickness. After cutting, the specimens were placed in a desiccator for several days prior to experimentation. The compositions of the propellants are given in Tables 1 - 6 and are taken from manufacturer-supplied data sheets where it is customary to list the volatile components separately, presumably because of changes during storage. Test specimens from each lot were prepared by cutting the cylindrical strands perpendicular to the axis of extrusion. This results in heat flowing along or parallel to the extrusion axis. When M30 is extruded, the needle-like nitroguanidine crystals line up in the direction of extrusion. To see what effect this alignment might have on heat conduction, an M30 specimen was also prepared by cutting a specimen wafer and number of 1-mm-thick slabs parallel to the extrusion axis. The 1-mm-thick slabs were stacked to form a specimen back-up piece. Thermal contact resistance between these slabs had been found to be negligible by Miller and Kotlar (1993), a fact which justifies use of the composite specimen. Thus, the conductivity and diffusivity of M30 were measured in directions both parallel to and normal to the extrusion axis.

**Table 1. M10 Composition (Lot No. RAD-PE-792-85, Packed 5/90)**

<u>CONSTITUENT</u>	<u>WEIGHT PERCENT</u>
	(Actual)
Nitrocellulose (13.12% N)	97.64
Potassium Sulfate	1.29
Diphenylamine	1.07
TOTAL	100.00
(Total Volatiles)	(8.73)

**Table 2. M9 Composition (Lot No. RAD-PE-792-77, Packed 2/90)**

<u>CONSTITUENT</u>	<u>WEIGHT PERCENT</u>
	(Actual)
Nitrocellulose (13.29% N)	57.62
Nitroglycerin	40.02
Ethyl Centralite	0.73
Potassium Nitrate	1.63
TOTAL	100.00
(Total Volatiles)	(0.26)

**Table 3. JA2 Composition (Lot No. RAD-PE-792-68, Packed 5/89)**

<u>CONSTITUENT</u>	<u>WEIGHT PERCENT</u>
	(Actual)
Nitrocellulose (13.04% N)	58.21
Nitroglycerin	15.79
Diethylene Glycol Dinitrate	25.18
Akardit II	0.74
Magnesium Oxide	0.05
Graphite	0.03
TOTAL	100.00
(Moisture Content)	(0.34)

**Table 4. M30 Composition (Lot No. RAD-PE-792-82, Packed 2/90)**

<u>CONSTITUENT</u>	<u>WEIGHT PERCENT</u>
	(Actual)
Nitrocellulose (12.68% N)	28.71
Nitroglycerin	22.02
Nitroguanidine	47.34
Ethyl Centralite	1.58
Cryolite	0.35
TOTAL	100.00
(Total Volatiles)	(0.67)



**Table 5. XM39 Composition (Lot No. IH-XM39-0988-100 A1, Packed 9/88)**

<u>CONSTITUENT</u>	<u>WEIGHT PERCENT</u>
	(Nominal)
RDX (5 micron)	76.0
Cellulose Acetate Butyrate	12.0
Nitrocellulose (12.6% N)	4.0
Acetyl Triethyl Citrate	7.6
Ethyl Centralite	0.4
TOTAL	100.0
(Total Volatiles)	(0.14)

**Table 6. M43 Composition (Lot No. IH-HELP1-0988-131 B1, Packed 9/88)**

<u>CONSTITUENT</u>	<u>WEIGHT PERCENT</u>
	(Nominal)
RDX (5 micron)	76.0
Cellulose Acetate Butyrate	12.0
Nitrocellulose (12.6% N)	4.0
Energetic Plasticizer	7.6
Ethyl Centralite	0.4
TOTAL	100.0
(Total Volatiles)	(not available)

#### 4. RESULTS

For each propellant at each different temperature, five runs were averaged to obtain the best value of conductivity and diffusivity at that temperature. The average values along with their standard deviations are given in Tables 7 and 8. Parabolic least-squares fits to these data are shown along with the data in Figs. 2 - 7, and the fitting parameters are collected in Tables 9 - 10. Error bars shown in the figures are the 5-run standard deviations. For M30, heat transfer along the extrusion axis proved to be about one third faster than in a direction normal to the extrusion axis, no doubt due to conduction enhancement afforded by alignment of the needle-like nitroguanidine crystals parallel to the extrusion axis. The microstructure of the other propellants is nearly isotropic so the conductivities are presumed to be isotropic. For this reason no subscript is used to denote direction for samples other than M30, even though measurements were made only along the extrusion axis. By comparing the values for thermal conductivity and diffusivity measured with the present technique to literature values for polymethylmethacrylate and Pyrex, Miller and Kotlar (1993) estimated that the technique provides an accuracy of  $\pm 5\%$  for materials with properties between these standards. The results reported here all satisfy this condition.

For convenience the polynomial fits to previously reported measurements (Miller (1992a)) of specific heats of specimens from the same six lots are given in Table 11. Estimated accuracy for these data is also  $\pm 5\%$ .

<b>TABLE 7. <math>10^4 \times</math> Thermal Conductivity (cal/cm-s-°C)</b> (⊥ indicates normal to extrusion axis, // indicates parallel to extrusion axis)						
Temperature	M10	M9	JA2	M30 <sub>⊥</sub>	M30 <sub>//</sub>	XM39
- 19°C	6.66 ± 0.34	no data	7.06 ± 0.59	no data	10.0 ± 0.5	6.12 ± 0.25
- 18°C	no data	6.61 ± 0.41	no data	7.87 ± 0.16	no data	no data
2°C	no data	no data	no data	8.41 ± 0.23	no data	no data
3°C	7.36 ± 0.27	7.06 ± 0.34	6.98 ± 0.50	no data	11.6 ± 0.7	6.34 ± 0.27
22°C	no data	no data	6.94 ± 0.29	no data	10.2 ± 0.6	5.86 ± 0.20
23°C	7.50 ± 0.28	7.08 ± 0.22	no data	no data	10.7 ± 0.6	no data
24°C	no data	no data	no data	7.64 ± 0.80	no data	no data
48°C	7.26 ± 0.35	no data	no data	7.76 ± 0.52	no data	5.88 ± 0.24
49°C	no data	6.92 ± 0.15	6.70 ± 0.27	no data	9.84 ± 0.38	no data

<b>TABLE 8. <math>10^3 \times</math> Thermal Diffusivity (cm<sup>2</sup>/s)</b> (⊥ indicates normal to extrusion axis, // indicates parallel to extrusion axis)						
Temperature	M10	M9	JA2	M30 <sub>⊥</sub>	M30 <sub>//</sub>	XM39
- 19°C	1.79 ± 0.07	no data	1.62 ± 0.11	no data	2.34 ± 0.09	1.54 ± 0.03
- 18°C	no data	1.49 ± 0.07	no data	1.78 ± 0.03	no data	no data
2°C	no data	no data	no data	1.74 ± 0.04	no data	no data
3°C	1.81 ± 0.05	1.44 ± 0.07	1.45 ± 0.08	no data	2.41 ± 0.14	1.50 ± 0.04
22°C	no data	no data	1.30 ± 0.05	no data	1.90 ± 0.09	1.32 ± 0.04
23°C	1.79 ± 0.04	1.33 ± 0.03	no data	no data	2.09 ± 0.11	no data
24°C	no data	no data	no data	1.46 ± 0.11	no data	no data
48°C	1.55 ± 0.05	no data	no data	1.39 ± 0.08	no data	1.21 ± 0.04
49°C	no data	1.31 ± 0.03	1.30 ± 0.03	no data	1.88 ± 0.04	no data

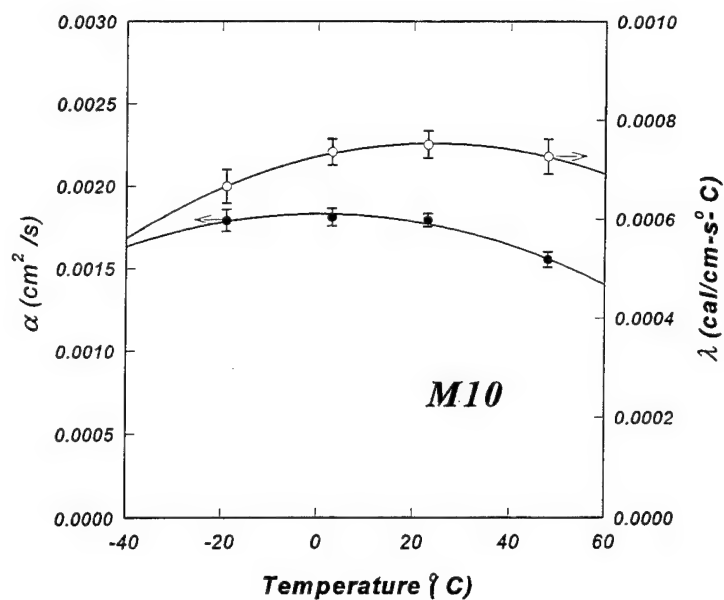


Figure 2. Thermal conductivity data (open circles, right scale), thermal diffusivity (solid circles, left scale), and their least-squares second-degree polynomial fits (line) for M10 homogeneous single-base propellant.

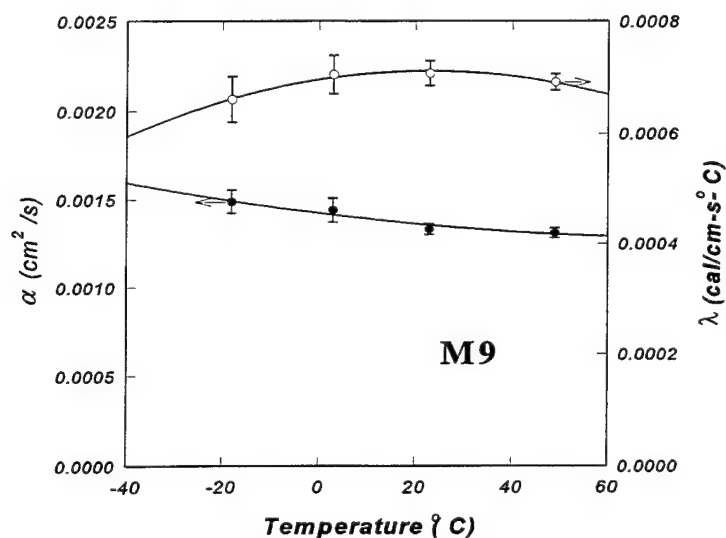


Figure 3. Thermal conductivity data (open circles, right scale), thermal diffusivity (solid circles, left scale), and their least-squares second-degree polynomial fits (line) for M9 homogeneous double-base propellant.

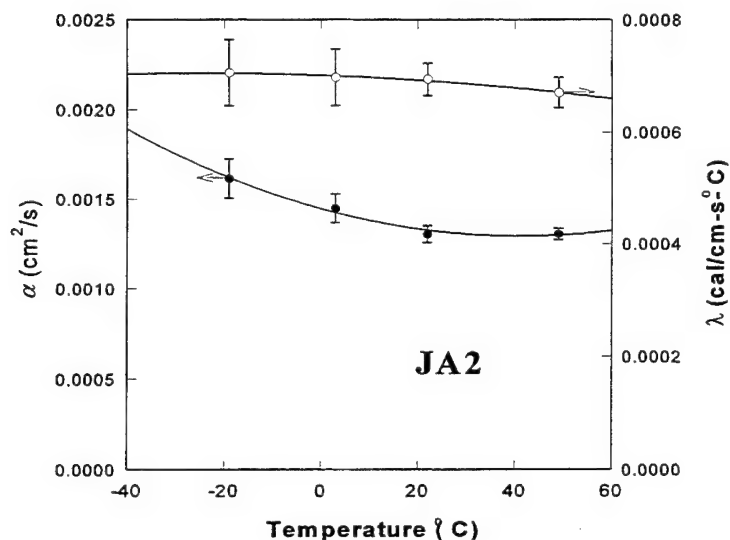


Figure 4. Thermal conductivity data (open circles, right scale), thermal diffusivity (solid circles, left scale), and their least-squares second-degree polynomial fits (line) for JA2 homogeneous triple-base propellant.

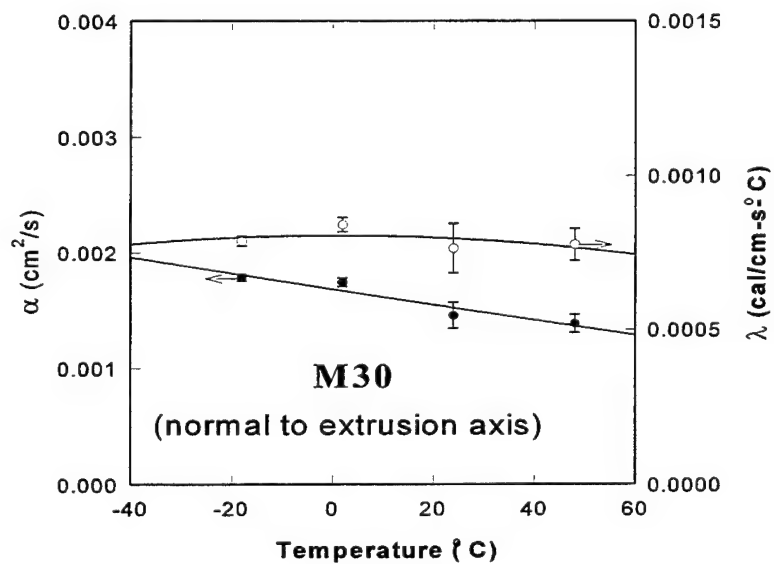


Figure 5. Thermal conductivity data (open circles, right scale), thermal diffusivity (solid circles, left scale), and their least-squares second-degree polynomial fits (line) for M30 composite triple-base propellant, for heat flow in a direction *normal to the extrusion axis*.

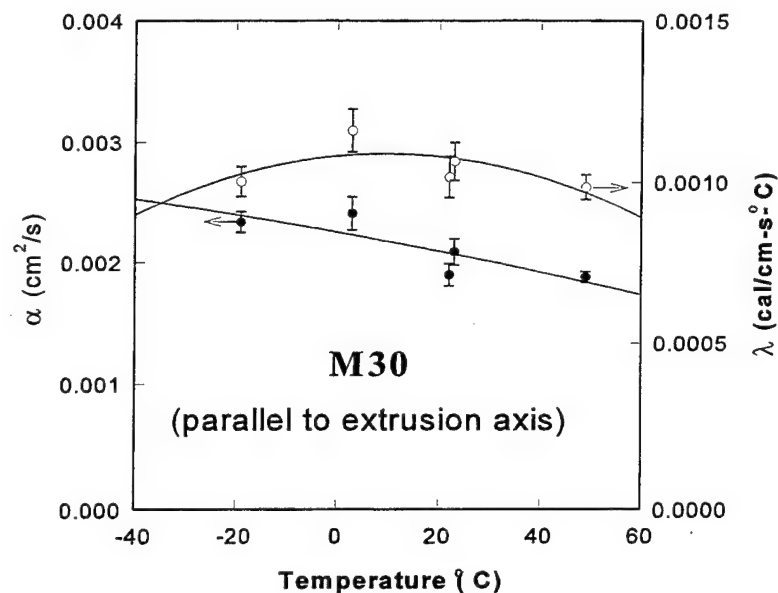


Figure 6. Thermal conductivity data (open circles, right scale), thermal diffusivity (solid circles, left scale), and their least-squares second-degree polynomial fits (line) for M30 composite triple-base propellant, for heat flow in a direction *parallel to the extrusion axis*.

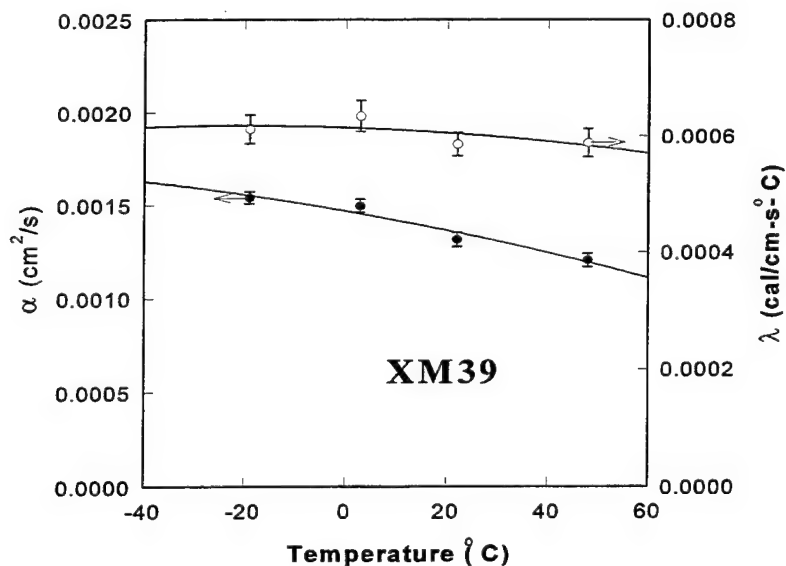


Figure 7. Thermal conductivity data (open circles, right scale), thermal diffusivity (solid circles, left scale), and their least-squares second-degree polynomial fits (line) for XM39 composite nitramine propellant.

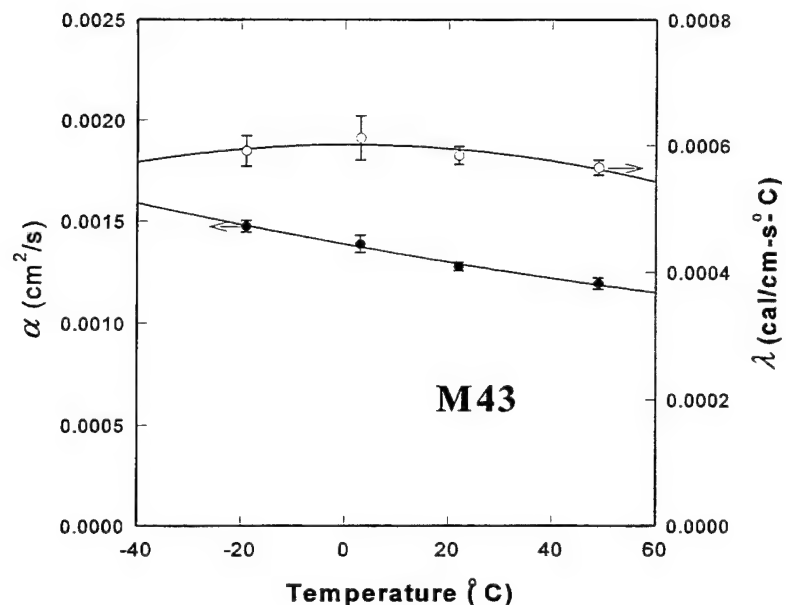


Figure 8. Thermal conductivity data (open circles, right scale), thermal diffusivity (solid circles, left scale), and their least-squares second-degree polynomial fits (line) for M43 composite nitramine propellant.

**TABLE 9. Polynomial Fits of Thermal Conductivity  $\lambda$**

(LEAST-SQUARES FITS)

$$\lambda(\text{cal/cm-s-}^\circ\text{C}) = f_0 + f_1T + f_2T^2, \text{ for } T \text{ in } (-20, +50^\circ\text{C})$$

( $\perp$  indicates normal to extrusion axis, // indicates parallel to extrusion axis)

Coefficient	M10	M9	JA2	M30 $\perp$	M30 $//$	XM39	M43
$f_0$	7.263E-4	6.971E-4	7.012E-4	8.058E-4	1.082E-3	6.147E-4	6.011E-4
$f_1$	2.243E-6	1.357E-6	-3.064E-7	1.827E-8	1.461E-6	3.080E-7	2.146E-8
$f_2$	-4.716E-8	-3.017E-8	-6.363E-9	-1.756E-8	-7.766E-8	7.351E-9	-1.669E-8

**TABLE 10. Polynomial Fits of Thermal Diffusivity  $\alpha$** 

(LEAST-SQUARES FITS)

$$\alpha(\text{cm}^2/\text{s}) = f_0 + f_1T + f_2T^2, \text{ for } T \text{ in } (-20, +50^\circ\text{C})$$

( $\perp$  indicates normal to extrusion axis, // indicates parallel to extrusion axis)

Coefficient	M10	M9	JA2	M30 $\perp$	M30 $//$	XM39	M43
$f_0$	1.831E-3	1.426E-3	1.447E-3	1.683E-3	2.252E-3	1.470E-3	1.387E-3
$f_1$	1.218E-7	-3.449E-6	-7.491E-6	-6.790E-6	-7.603E-6	-4.781E-6	-4.605E-6
$f_2$	-1.207E-7	2.003E-8	9.095E-8	3.323E-9	-1.722E-8	-1.979E-8	1.124E-8

**TABLE 11. Polynomial Fits of Specific Heat  $c_p$** 

(LEAST-SQUARES FITS)

$$c_p(\text{cal/g-}^\circ\text{C}) = f_0 + f_1T + f_2T^2 + f_3T^3 + f_4T^4, \text{ for } T \text{ in } (-40, +75^\circ\text{C})$$

Coefficient	M10	M9	JA2	M30	XM39	M43
$f_0$	2.404E-1	2.987E-1	3.003E-1	2.887E-1	2.496E-1	2.487E-1
$f_1$	7.831E-4	7.728E-4	8.128E-4	8.434E-4	7.25E-4	7.639E-4
$f_2$	3.821E-6	1.031E-6	1.057E-6	4.800E-7	1.575E-6	4.105E-7
$f_3$	5.201E-8	1.700E-7	1.552E-7	1.017E-7	6.144E-8	4.129E-8
$f_4$	-9.439E-10	-2.278E-9	-2.190E-9	-1.537E-9	-9.142E-10	-5.334E-10



## 5. CONCLUSIONS

Thermophysical properties are required for a wide range of ignition and combustion calculations and yet few measurements of these properties have been published for solid propellants. This report documents such measurements for six U. S. Army solid gun propellants over the temperature range  $-20^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$  using a newly developed technique for the simultaneous determination of thermal conductivity and diffusivity of small test specimens. The accuracy of these measurements, including previously measured specific heats, is estimated to be  $\pm 5\%$  and least-squares polynomial fits of these data are provided as a function of temperature for convenience in calculations.

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